

THE PRODUCTION AND EVALUATION OF OILS FROM THE STEAM PYROLYSIS OF POPLAR CHIPS

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INTRODUCTION

In the early 1970's, as a response to the world oil crisis, two water-based technologies for the thermal liquefaction of woody biomass were studied extensively. The first of these, based on Bergstrom's earlier work (1), employed sodium carbonate as a soluble catalyst, and carbon monoxide as a reducing gas (2,3). The second technology, also based on earlier work, used nickel metal catalysts and hydrogen (4). In all cases the substrate was powdered wood slurried in water, and, in those studies using nickel metal as catalyst, it was not clear what role the catalyst played. In particular it was realised that the wood must yield gases or liquid before the catalyst could intervene. If liquids were formed, then the role of the catalyst/hydrogen system would be stabilisation, since under moderate heating rates, biomass alone in water does not yield significant quantities of oil. The stabilisation could also involve upgrading, if such things as oxygen content and viscosity were also decreased.

In subsequent experiments (5) we semi-continuously fed slurries of powdered wood along with nickel carbonate and hydrogen to a reactor. The feed, on entering the reactor, was heated sufficiently rapidly that the nickel carbonate decomposed to nickel oxide instead of reducing to nickel metal. In addition, when product was discharged from the reactor, both char and oil--the latter in 25 per cent yield--were present. We reasoned that the oil yield was initially higher, but that, because of the unavoidable, prolonged residence time up in the reactor, and the absence of the stabilising system (no nickel metal), some of the oil had charred.

As a test of this theory, powdered wood was heated rapidly, together with only water, in small reactors to 350°C, and then quenched (6). Oil yields (acetone-soluble) in up to 50 per cent by weight were obtained.

Until this time, all studies in both technologies had been confined to powdered wood or sawdust, the general opinion being that heat and mass transfer limitations in larger wood pieces would prevent liquefaction. However, we studied the liquefaction of single poplar chips (6.5 mm square cross section) in the same small reactors, and showed they were completely liquefied at 300°C and above (7). Steam entered the chips, swelling them and disrupting the matrix. The oil which was formed appeared to be stabilised by the presence of liquid water. The chemical conversions were obviously delayed relative to powdered wood, and some poplar clones yielded up to 6 per cent phenol from the chips, but not from the powdered form. Scanning electron microscopy showed liquefaction at the cellular level (8,9). On the surface the middle lamella merged with the cell walls and the matrix then flowed and engulfed the cells. Inside the chips, spherical structures appeared, particularly on the walls of vacuoles. These structures eventually filled irregular cavities which formed in the matrix. Gas or vapour bubbles could also be seen in the flowing matrix.

On the basis of these results it was decided that a laboratory unit should be constructed for the purpose of studying commercial-size (and larger) chips. The overall unit is shown schematically in Figure 1.

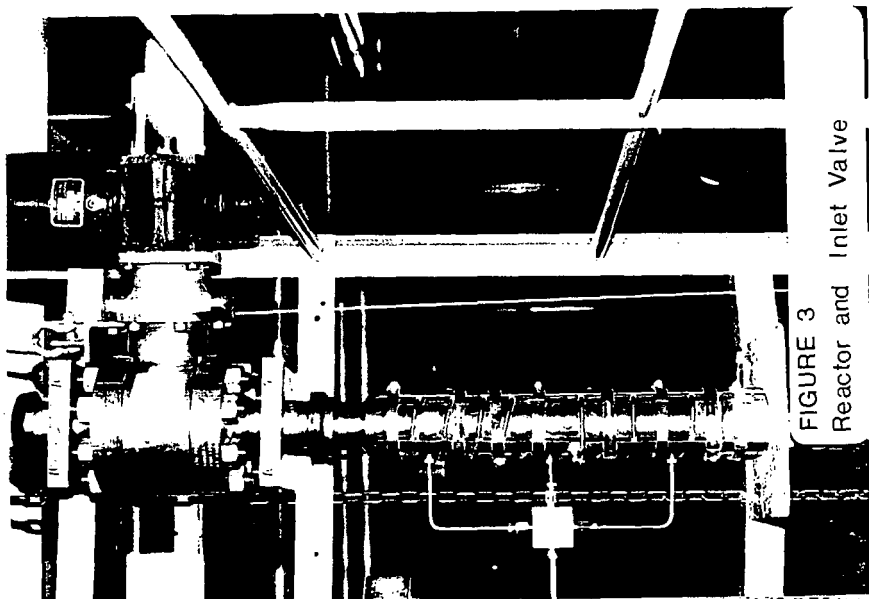
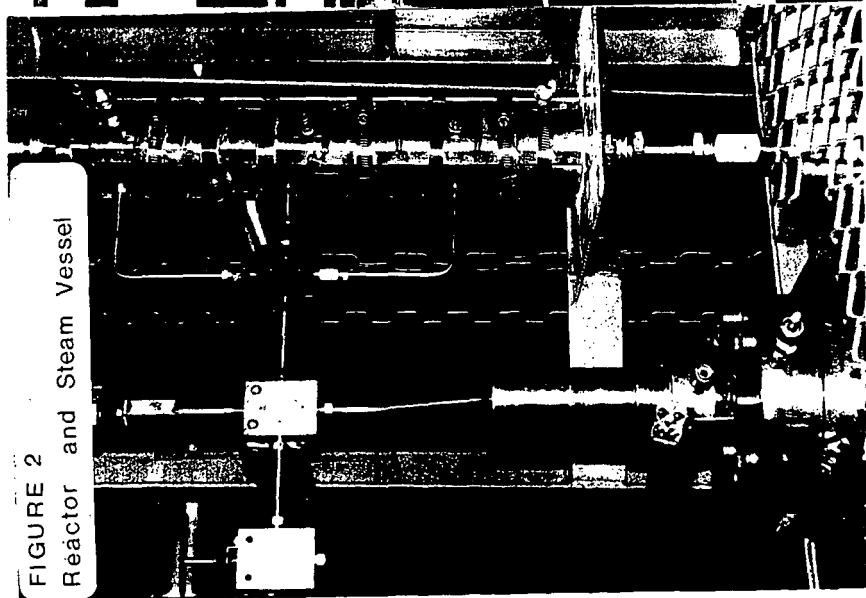


FIGURE 1 CASCADE UNIT FOR
WOOD CHIPS LIQUEFACTION

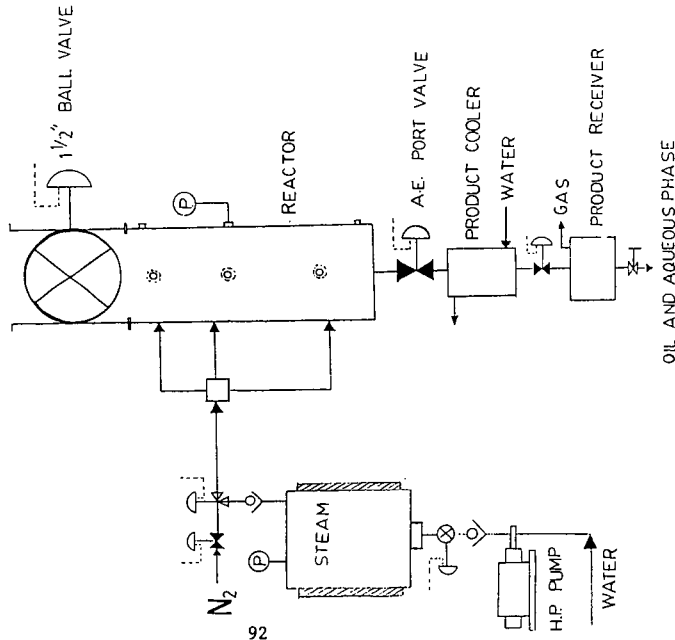
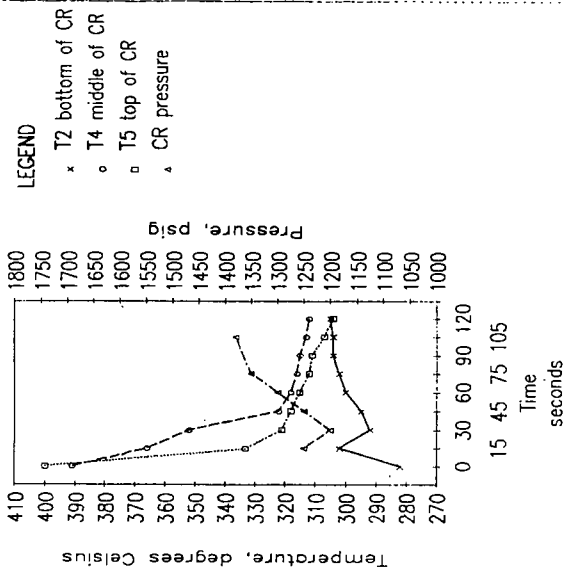


FIGURE 4
Temperature, Pressure Profiles

Steam for 7 Seconds
340 C, 2100 psig
1.0 L Water in SG



The Reactor

The reactor (Figures 2 and 3) was designed by THP Inc. according to ASME Code, Section VIII, Div. I., 1984 addenda. The rating was set at 24.1 MPa (3500 psi) at 350°C which allowed for 7.6 MPa (1100 psi) gas overpressure above the vapour pressure of water 16.5 MPa (2400 psi) at that temperature. A single ingot of TP 316 stainless steel was used for machining the reactor which has an internal diameter of 1.5 inches (3.8 cm) and an external diameter of 3.0 inches (7.6 cm). The length is 19 inches (48 cm) and the internal diameter is 600 mL which allows for a feed of 100 g of dry wood chips. At the top end an Oteco hub (Figure 2) is threaded and seal welded to the reactor body. A 1 inch Autoclave Engineering (AE) slim-line connector is threaded to the base of the reactor. A total of 9 holes are drilled in the reactor body to take 1/4 AE inch-slim connectors. The three on the left side of the reactor are for steam inlet lines. On the front face the top hole is for a rupture disc (20.67 MPa, 3000 psi). The middle hole is for a 1/8 inch thermocouple, and the bottom hole is for a vent line. On the right hand side, the upper and lower holes are for 1/8 inch thermocouples, and the middle hole is for a pressure gauge.

The reactor is clamped near its base by a split ring which is spot welded to a bracket bolted to the reactor frame. The split ring also supports a steel plate on which insulation, in the form of ceramic brick, (not shown in Figures) is stacked to the neck of the reactor. The brick is cut and fitted to the external contours of the reactor. A rectangular steel case is fitted outside the brick.

Heating is supplied to the reactor by two, 6 feet long (1.8 inch O.D.) heaters joined in parallel. These are coiled around the reactor as shown in Figures 2 and 3, and held close to the reactor by four longitudinal steel strips and eight circlips. The maximum power drawn by the heaters is 4 kw. The coils are operated through a temperature controller and with all the lagging in the place, the reactor can be brought to 365°C in 70 minutes.

Inlet Valve and Feed Basket

The inlet valve and its relationship to the reactor can be seen in Figure 3. The valve (Mogas Industries Inc.) is a 1.5 inch (3.8 cm) ball valve (ANSI 2500 series) rated at 24.8 MPa (3600 psi) at 370°C. It is joined to the reactor by a matching Oteco hub and supported on the frame by two brackets. The controller is air operated via solenoid valves. Failure of air pressure closes the valve. The valve is insulated by three layers of 1.5 inch thick glass wool, thus preventing excessive heat losses. The valve and controller together weigh 68 Kg and are attached to a pulley system to facilitate removal from the reactor when this is necessary.

The cylindrical feed basket is made of stainless steel mesh and is spot welded. The basket, besides facilitating feed addition, prevents contact of chips with the reactor walls and allows recovery of unconverted wood.

Outlet Valve

Another 1.5 inch ball valve was originally planned for the reactor outlet. However, because of initial cost considerations, this was replaced with a Crosby 0.5 inch ball valve (ANSI 1500) rated at 18.4 MPa (2665 psi) at 370°C. Special hubs were made by THP for connection to the reactor and the cooling lock. Considerable leaks were encountered with this system, probably because of misalignment of the hubs with the reactor body. Therefore, the system was replaced with a 0.5 inch AE seat and cone (port) valve rated 17000 psi at 350°C. The products thus had to negotiate two right angle turns before entering the product cooler. However, this was not considered a problem, because only water, oil and finely divided material would be exiting the reactor. The Crosby valve may be retested in the future after modification of the hubs.

Let-Down Lock and Collection Vessel

The cooling lock is a 20 inch long AE nipple, having an internal diameter of 0.688 inches (1.7 cm). The internal volume is 122 mL. An external copper jacket allows for use of a coolant, although at this time air cooling appears to be sufficient. Indeed excessive cooling is not desirable as the oil may not flow easily to the product collection vessel. At the time of writing, we are planning the installation of a larger lock (300 mL), since the total liquid discharge often exceeds the volume of the present lock.

The products discharge from the lock into a pyrex cylindrical vessel, approximately 5 inches in diameter and about 8 inches deep. Another smaller container such as a beaker can be placed inside the vessel if necessary. The collection vessel is sealed except for an outlet for the product gases which pass to a brine displacement vessel for volume measurement.

Steam Vessel and Injection

The top of the steam generator is visible at lower left in Figure 2. It is a 2 L AE autoclave equipped with a pressure gauge and thermocouple. The magne drive stirrer has been left in place but is not used. The steam transfer line can be seen passing upward from behind the magne drive to a two-way valve. When the steam line is closed, nitrogen flush gas can be passed from the transfer line on the left hand side to the reactor. Steam and nitrogen enter the reactor at three locations on the reactor as shown (Figure 2). If necessary, the hot generator can be charged with make up water using a Milton Royal high-pressure pump.

Control Panel and Safety Systems

The control panel is located in a room directly adjacent to that containing the unit. The panel contains main switches as well as switches to open and close the various valves. A digital readout and/or chart indicators allow the monitoring of thermocouple temperatures.

The major hazard of this type of equipment is the accidental release of steam to the atmosphere with subsequent injury to personnel. The equipment does contain an electrical override, in that the steam inlet valve can not be electrically operated, unless closure of the reactor inlet valve is initiated. However, this is not sufficient, since the reactor inlet valve takes 3-4 seconds to close, whereas the steam inlet valve opens in about 1 second. Thus if the switch for the steam inlet valve is moved to the open position immediately after the switch for the reactor inlet valve is moved to the closed position, then the contents of the steam vessel could discharge through the inlet valve. The system has, therefore, been provided with an extra safeguard in that the shaft of the inlet valve actuator now carries an extension arm. When the valve is fully closed, the extension arm activates a microswitch which only then allows the steam inlet valve to open. The equipment is also designed such that the main inlet valve cannot be opened if the steam valve is open. This is a purely electrical override but is sufficient, since the steam valve operates faster; i.e., it closed much faster than the reactor inlet valve can open. This, however, does not prevent the accidental discharge of the reactor contents to the atmosphere. To avoid this possibility, the reactor inlet valve has a keyed switch. The operator, after manually loading the wood, then inserts the key to close the reactor inlet valve. He then removes the key rendering the switch inoperable.

Polymethylmethacrylate sheet is installed around the equipment in locations where sudden steam leaks could otherwise injure the operators.

Operation of the Unit (Experimental)

Figure 4 shows typical temperature and pressure profiles (340°C steam injected

for 7 s). Before steam injection, the top and middle of the reactor had temperatures close to 400°C whereas the bottom of the reactor, where heat losses are greater, was at 300°C. After steam injection, the temperatures shown by the upper two thermocouples dropped over a period of about 2 minutes and came close to the temperature of the bottom thermocouple. Condensed steam was present in the base of the reactor, and the internal pressure of the reactor was controlled by the temperature of the surface of this water plus nitrogen and product gas overpressure. As might be expected, the pressure in the reactor is slightly higher than the equilibrium steam pressure corresponding to the temperature of the thermocouple at the base of the reactor (i.e., at the bottom of the water layer).

The following procedure is typical for a liquefaction experiment. The reactor was preheated and flushed with nitrogen with the inlet valve open. The stainless steel basket was loaded with wood chips (100 g, 8 per cent moisture) and then quickly lowered through the inlet valve. The nitrogen valve was closed, as was the inlet valve. Immediately the steam line was opened--usually for about 7 s. After 2 minutes, the products were discharged into the cooling lock, and after a further 30 s the valve to the collection vessel was opened. The gas separated and its volume was measured by displacement of water. Temperatures and pressures in the reactor and steam vessel were monitored throughout this procedure. The basket was retrieved through the inlet port after venting of the reactor.

The oil solidified and could be physically separated from the water by filtration (acetone free oil). The aqueous layer was centrifuged to yield a small insoluble fraction (aqueous-phase solids) most of which was acetone-soluble. An acetone flush of the reactor yielded further oil (acetone-wash oil). A small amount of acetone-insoluble material stuck to the walls of the basket (insolubles). The moisture content of the acetone-free oil was about 20%. However, heating the oil to 70°C for half an hour lowered the water content to less than 3%. This is a rather dramatic, and unexpected reduction in water content, but remelting the oil allows the separation and evaporation of water that was trapped when the oil originally solidified. This semi-dry oil softened around 50°C.

RESULTS AND DISCUSSION

The results from one typical run are discussed here. A steam temperature of 355°C was used, and the wood chips in this instance were soaked for 20 minutes with water for 20 minutes prior to addition. A further 51 g of water was added to the reactor in this way. The presoaking, which was intended to prevent charring, has no advantages and has now been discontinued.

A reasonable, overall mass balance was obtained, but this was not very meaningful, given the relatively large amounts of water involved in the reaction. Approximately 250 g of water were discharged in this run, and no particular effort was made at that time to limit the amount of condensate. A more important aspect is the carbon balance, and in this run slightly more carbon (45.6 g) was accounted for in the products than was in the feed (44.4 g). Figure 5 shows the distribution of carbon in the various product phases. The insoluble fraction is a composite of those acetone insolubles left on the basket and those in the oils. No aqueous phase acetone-insoluble solids were obtained with 355°C steam, and they only become significant when using steam below 340°C. The fraction of total carbon in the gas phase was close to 10 per cent. As in previous runs, about 90 per cent of this gas was carbon dioxide--the balance being mostly carbon monoxide. The total mass of gas was 18.6% of the wood mass. From our previous work on single chip (0.64 x 0.64 x 7.6 cm) liquefaction (7) this is approximately the percentage that would be produced at a water/wood ratio of 1.0 when the steam is generated internally. In that case, however, the oil chars due to the lack of water, so the mechanism for the increased gas production is probably different.

The elemental composition of the oil are also very similar to those obtained in

FIGURE 5
Wood Chips Liquefaction
Carbon Distribution in Products

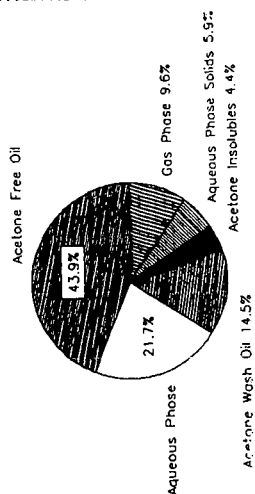
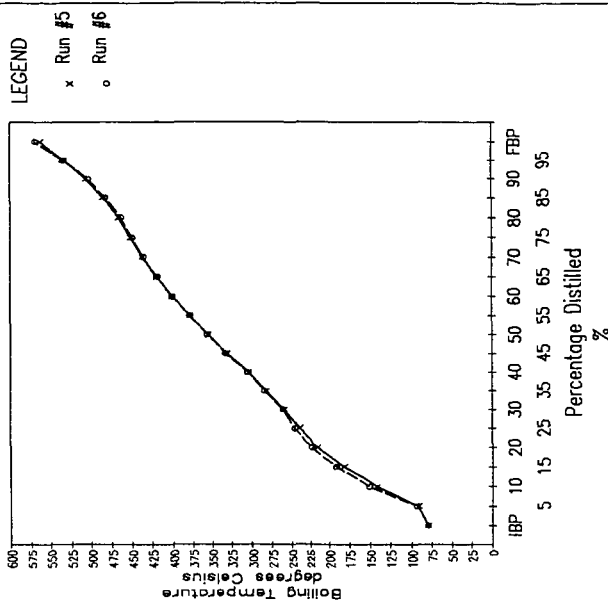


FIGURE 6
Boiling Point Distribution
of Acetone Free Oils
by ASTM Method D2887-73



Data provided by DC Research

the previous study, the carbon percentage being close to 70.0 and the hydrogen being around 6.5. The oxygen percentage (by difference) is thus in the low 20 per cent range. If complete oxygen removal was required by hydrotreating, then the viable oxygen limit in the substrate from an economic standpoint is about 20 per cent (11).

A distillation curve for the oils is shown in Figure 6. Approximately 60 per cent of the oil distills below 405°C, which is at the upper end of the range for heavy gas oil in petroleum distillation. Although the average molecular weight of the oil is not known at this time, it can be estimated from Goring's work (10) on the softening point of lignins that the value is less than 1000. The distillation results and the polar nature of the oil (which would increase boiling points relative to alkanes of similar molecular weight) support this estimation.

Continuing Work

Experiments are continuing to define the optimum temperatures and residence times for maximising oil yield and quality. In addition, the effect of water content and chip size are being investigated. Further results from these studies will be reported in the near future.

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